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High-Efficiency Steam Electrolyzer

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HIGH-EFFICIENCY STEAM ELECTROLYZER

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Abstract

We are developing a novel high-efficiency, high-temperature steam electrolyzer. Although water or steam electrolysis is well known to be one of the cleanest ways to produce hydrogen, widespread utilization is hindered by high operational costs because of high electricity consumption. To decrease the electrical power input requirements in electrolysis, our approach uses natural gas as an anode depolarizer. This approach essentially replaces one unit of electricity with one equivalent-energy unit of natural gas at much lower cost. The direct use of natural gas on the electrolyzer enables very high system efficiency with respect to primary energy. Experiments performed on single cells have shown a voltage reduction as much as 1 V when compared to conventional electrolyzers. System efficiency has been estimated to be 50 to 80%, depending on the electrolytic current. A 200-W prototype unit is being developed.

Introduction

Currently, most hydrogen demand is met by hydrogen production from fossil fuels, i.e., by steam reforming of natural gas and by coal gasification. However, most of these central plants are located in remote areas. The hydrogen produced must then be delivered to the users either by truck or via hydrogen pipelines. Because of the inherently low energy density of hydrogen, transportation by truck is not a viable option. Hydrogen delivery using pipelines is not cost-effective either because of the high cost of the pipelines (about $1 million/mile). Therefore, hydrogen production for a future hydrogen economy is likely to be accomplished using a

distributed system where hydrogen is produced close to where it is consumed. A distributed hydrogen production system using small conventional steam-reforming reactors is not feasible because of the very high cost of the reactors at small scales. More interesting approaches, such as auto-thermal reforming as well as partial oxidation processes, are currently being pursued. However, these approaches are fairly complex, involving several additional steps, such as high-temperature shift, low-temperature shift, and preferential oxidation or hydrogen gas separation.

Hydrogen can be produced from water or steam electrolysis using much simpler technology. Because of the modularity of the electrolyzer, electrolysis can be done at a large central plant, at a refueling station, or even at home. In addition, electrolysis using renewable electricity offers the possibility of producing hydrogen without any greenhouse gas emissions. However, water electrolysis has not had a significant commercial impact because it has not been cost-effective.

The main drawback of conventional electrolyzers is the high electricity consumption. Electricity from the typical grid is known to be by far the most expensive form of energy. As a result, electrolytic hydrogen is more expensive than the steam-reformed hydrogen by a factor of at least two to three (Donitz 1980, Donitz 1985, Donitz 1990). Moreover, electricity is not a primary energy but must be produced using fossil fuels, nuclear fuels, or renewable energy. Considering the fact that production of electricity has an average efficiency of less than 40% with respect to primary energy, the overall efficiency of the electrolyzer in general is below 40% (Donitz 1990). In addition, less than 20% of the overall electricity production in the United States uses renewable energy. As a consequence, electrolysis using electricity from the grid is not a carbon-free process but actually involves the production and release of large amounts of greenhouse gases. From this viewpoint, conventional electrolysis is probably the worst hydrogen production technology in terms of greenhouse-gas emissions. On the other hand, electrolysis using exclusively renewable energy would have limited applications because it must be linked directly to a renewable energy source.

Recently, we have developed a new approach to reduce the electricity consumption in electrolyzers (Pham, 2000). Reduced electricity consumption was achieved by using natural gas to reduce the chemical potential difference across the electrolyzer cell. The concept is called Natural-Gas-Assisted Steam Electrolysis (NGASE). Although NGASE still involves carbon emissions because of the use of natural gas, the high efficiency and the simplicity of the system make it attractive as a hydrogen production technology for the transitional phase toward the hydrogen economy.

The goal of this project is to develop a prototype 1-kW-equivalent NGASE system for technology validation in 2006.

Concept

In conventional steam electrolyzers, the gas supplied to the cathode side (where water is decomposed) is usually a mixture of steam and hydrogen, while the gas supplied to the anode side is usually air. At zero current, the system has an open-circuit voltage of 0.8 to 0.9 V, depending on the hydrogen/steam ratio and on the operating temperature. In order to electrolyze

water, a voltage that opposes and is larger in magnitude than the open-circuit voltage must be applied to pump oxygen from the steam side to the air side. Clearly, much of the electricity used, 60 to 70% of the total electrical power, is "wasted" by forcing the electrolyzer to operate against the high chemical potential gradient for oxygen.

To lower the open-circuit voltage, and thereby the electricity consumption, our approach is to replace the air in the anode side with natural gas. The reducing character of natural gas helps to lower the chemical potential difference between the two sides of the electrolyzer. One can distinguish two different modes of operation: total oxidation or partial oxidation of natural gas. In the first case, natural gas is used in the anode side of the electrolyzer to burn out the oxygen resulting from the electrolysis, thus reducing or eliminating the potential difference across the electrolyzer membrane. The products of the reaction will be CO_2 and steam. High fuel utilization is required. The role of natural gas is just to lower the chemical potential gradient, and therefore the electricity consumption. This mode replaces one unit of electrical energy by one equivalent-energy unit of natural gas at one fourth the cost. Thermodynamics limits the operational temperature for the total oxidation mode to temperatures lower than 800°C. Above 800°C, carbon monoxide becomes more stable and total oxidation is not possible.

In the second operational mode, an appropriate catalyst on the anode side promotes the partial oxidation of natural gas to CO and hydrogen. The resulting gas mixture, also called syngas, can be used in important industrial processes such as the synthesis of methanol and liquid fuels. Most importantly, CO can also be shifted to CO_2 to yield additional hydrogen. In this process, hydrogen is produced at both sides of the steam electrolyzer. The overall reaction is equivalent to the steam reforming of natural gas. In contrast to steam-reforming reactors, the modular characteristics of the electrolyzer, together with the absence of the extensive heat exchangers, make it economically feasible to make small-scale hydrogen production units. However, the partial oxidation approach is much more complex than the total oxidation mode because it involves several additional reactor units, as described above for the steam-reforming process.

In both cases, the key point of the approach is to use natural gas directly in the electrolyzer instead of using natural gas to make electricity at the central plant. The efficiency will be higher, and the carbon emissions will be lower than in conventional electrolysis.

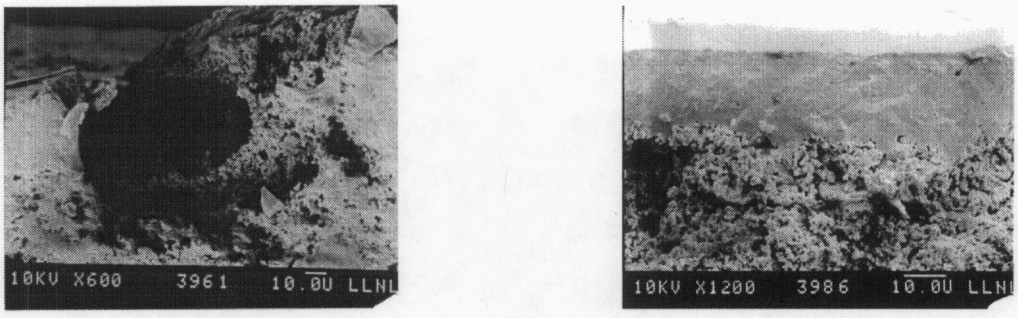
Summary of Previous Accomplishments

We have demonstrated the proof-of-concept of the NGASE approach using single disks. A voltage reduction of 1 V was observed when methane was used in the anode side. The electricity consumption was estimated to be about one order of magnitude smaller than in conventional electrolyzers. Using thin film and novel catalyst materials, we demonstrated very high performance, up to 1 A/cm^2 at only 0.5 V at 700°C. At 800°C, cell current was as high as 2.4 A/cm^2. For electrolyzer stack development, we selected the tubular approach since tubular structure has good mechanical integrity while enabling operation at high pressures. A tube fabrication process has been developed.

Accomplishments

Tube Fabrication

Making electrolyzer tubes is the single most important effort in the whole fabrication process of the NGASE stack. Since we have demonstrated the feasibility of the NGASE concept for small disk samples, the technical success of the project now depends largely on the scale-up—, i.e. the fabrication of the electrolyzer tubes. During FY00, we developed a laboratory-scale fabrication process to make tubes. However, the thin-film coating turned out to be extremely challenging. Indeed, although it is reasonably easy to fabricate defect-free thin films on small samples, the risk of having defects on large-size samples multiplies linearly with increasing area. The most detrimental defect is short-circuiting through the electrolyte coating because of the presence of pinholes. Even just one pinhole that causes short-circuiting in the electrolyzer renders the whole tube useless. The defects typically come from fabrication of the tube or from the coating itself. Figure 1 shows an example of a defect caused by the tube fabrication. A large hole can be seen on the surface of the tube. The presence of the hole causes disruption in the electrolyte coating. When the cathode is subsequently deposited (not shown in the picture), the cathode material can penetrate inside the coating and be in contact with the anode, causing short-circuiting. At first, we had a coating yield of less than 10% for 3-inche tubes.



a b

Figure 1: Cross section views of: a) pinhole defect on the tube surface; b) thin film electrolyte coating without defect even though there is a pinhole on the tube surface.

We have improved both the fabrication process to have less defects on the tube surface, and the coating process itself to make it less sensitive to tube defects. Figure 1b shows an example of a tube that has a surface pinhole. Using the improved coating process, we could deposit a defect free electrolyte film that actually covered the tube pinhole. The new process has a yield of 80%. We are working to further improve the yield rate. The short-circuiting problem was a major hurdle in the development of the prototype electrolyzer stack. This problem is now overcome.

Using the improved fabrication process, we have been able to make longer tubes, up to 6 inches in length. Figure 2 shows an example tubes at different steps in the fabrication process.

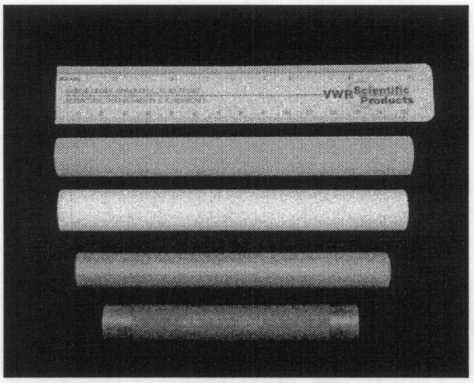


Figure 2: Pictures of tubes at different steps in the tube fabrication process

Performance Characterization

The electrolyzer tubes were submitted to several tests to evaluate the mechanical and electrochemical performances. Pressure tests indicated that the tubes survived up to 200 psi at room temperature and 85 psi at 700°C. The test at room temperature was limited to 200 psi because of the testing apparatus, not because of the tubes themselves. The test at 700°C was stopped at 85 psi because of leakage through the high temperature seals, which prevented further pressurization. With better seals, we expect to demonstrate tube survival above 150 psi at temperatures.

The tubes were also submitted to repeated temperature cyclings with ramp rate up to 20 °C/min. No degradation was observed.

Figure 3 shows the electrochemical performance of a single tube. Each tube produced about 30 and 70 sccm hydrogen from the cathode side (steam side) at 700 and 800°C respectively. In the partial oxidation mode where hydrogen is produced on both sides, the total hydrogen produced was 280 sccm. Tube performance is still only 30 % of disk data. Efforts to improved tube performance are planned for 2002.

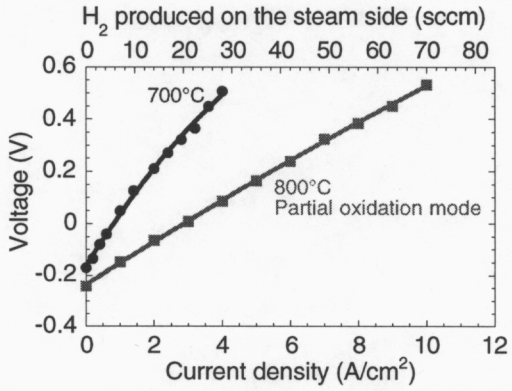


Figure 3: Electrochemical performance of single tube

Electrolyzer Stack Development

In FY2000, we selected the tubular configuration approach for the NGASE stack. The tubular stack design enables us to electrochemically compress hydrogen in the steam side while having natural gas at ambient pressure only inside the tube. This eliminates the need for a natural gas compressor. This year, we continued the development of the stack. In particular, the effort was focused on:

Seal Development

Due to the operation at high pressure-differential, conventional high-temperature ceramic and glass-ceramic seals barely meet the requirements. We thus selected the metal-to-ceramic brazing as sealant approach. Various brazing alloys were tested for their compatibility with the tube as well as with the alloy serving as interconnect. The best seal tested so far survived pressures up to 85 psi; beyond this threshold, seal leakage occurred. By further optimizing the thermal expansion matching between the different components, better seals can be developed. In a parallel effort, we are developing an engineering design that will eliminate the need for high temperature sealant.

Tube-To-Tube Series Connections

Each electrolyzer tube operates at high current, up to 70 A, and at a voltage lower than 1 V. In order to increase the voltage, we developed the tube-to-tube series connection approach. This approach is similar to the segmented-in-series originally developed for Solid Oxide Fuel Cells for similar purpose. However, due to the favorable environment in the electrolyzer case, as compared to the fuel cell case, metallic interconnect can be used to electrically connect tubes together. Figure 4 shows a picture of three tubes that are connected in series via the metal interconnects that were brazed to the tubes.

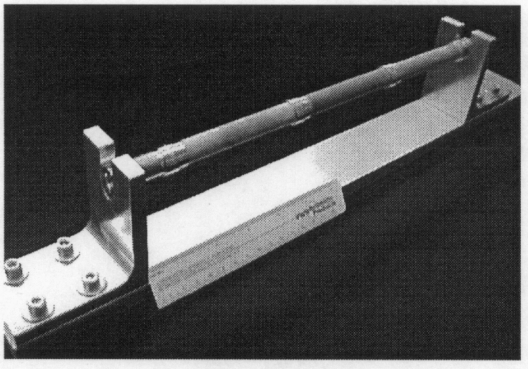


Figure 4: Three tubes with series connection

200 W Stack Development

We are currently working on the 200 W electrolyzer stack. Figure 5 shows the initial model of twelve tubes connected in series and in parallel; together with the metal vessel that will enable the operation at pressures up to 150 psi. Pressurization test of the bench scale reactor was accomplished.

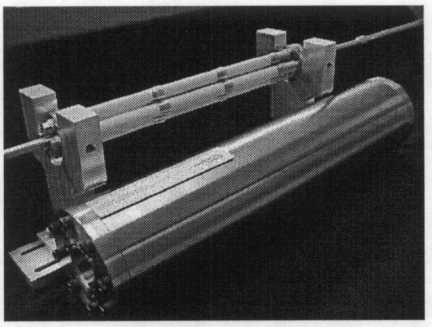


Figure 5: NGASE stack model with 12 tubes

System Analysis

Preliminary system design of the NGASE was completed for this phase. The result of the system analysis is illustrated in figure 6. The single cell data was used for analysis. Using an average efficiency of 40% for the grid, it is shown that, when properly designed, the electrolyzer efficiency is between 50 to 85% with respect to primary energy. Several factors, including the natural gas fuel utilization at the anode and the electrolytic current density, have strong influence on the system efficiency. The efficiency increases dramatically with decreasing electrolytic current. At a high current density of 1 A/cm^2, the efficiency would be 53% (80% fuel utilization, LHV) while at 0.4 A/cm^2, it is as high as 76%. However, capital cost consideration would impose a limit in how low the current density can be. The efficiency also increases with increasing consumption of natural gas in the anode. However, it will be difficult in practice to

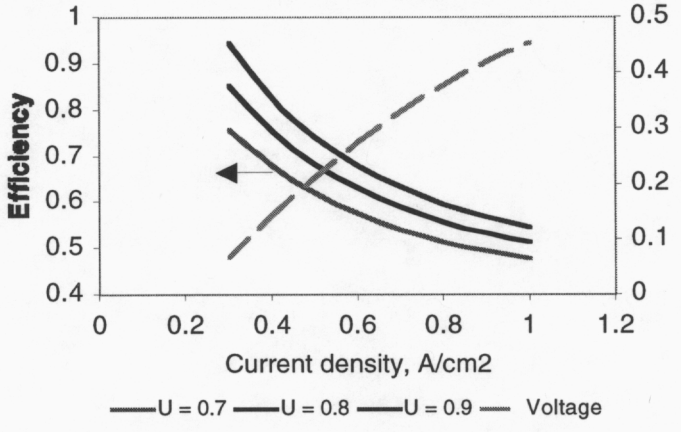


Figure 6: Efficiency as a function of current density at different fuel utilizations U

have a natural-gas utilization higher than 85%. Nevertheless, the analysis indicates that the NGASE can have much higher efficiency with respect to primary than the conventional electrolyzers, for which the efficiency is typically less than 40% (Donitz 1990). Compared to other reformer approaches, the NGASE has more operational flexibility since the efficiency and hydrogen production rate can be easily adjusted depending on the requirements.

Conclusion and Future Work

We have advanced considerably the development of the NGASE. The scale-up to larger size samples has encountered some difficulties that are typical in most scale-up effort. The coating problem has been overcome. The ground-work for stack development was accomplished. Preliminary system analysis indicates high efficiency, up to 80% can be achieved.

We will further improve the tube fabrication process in order to have tube performance close to that of single disks. Long-term stability will be evaluated. We will continue the system and process engineering to develop NGASE stacks. Our goal is to fully develop a NGASE prototype for technology validation in 2006. American Fuel Cell LLC (AFC), a private start-up company, has recently negotiated an exclusive licensing of our technology. AFC will work with us through a CRADA to bring this technology to commercialization. In particular, AFC will provide the manufacturing support that is much needed for the fabrication of kW size systems.

Acknowledgements

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References

Donitz, W., Schmidberger, R., Steinheil, E., Streicher, R., *Int. J. Hydrogen Energy*, **5**, 55 (1980).
Donitz, W., and E. Erdle, *Int. J. Hydrogen Energy*, **10**, 291 (1985).
Donitz, W., Erdle, E., Streicher, R., 1990. *Electrochemical Hydrogen Technologies.*, Wendt, H., Editor. Elsevier. p 213.
Pham, A.Q., H. Wallman, R.S. Glass, US patent n°6051125 (April, 2000).